SOME REACTIONS OF SULPHUR AND ITS OXIDES

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WILLIAM RALPH SKIDMORE

B.A., University of Oregon, 1920
M.A., University of Oregon, 1922

DISSERTATION

IN

CHEMISTRY

Submitted in Partial Fulfillment of the Requirements for the

DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE GRADUATE COLLEGE

OF THE

STATE UNIVERSITY OF IOWA

1925

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SOME REACTIONS OF SULPHUR AND ITS OXIDES

Introduction and Purpose

The reduction of sulphur trioxide has been studied in a qualitative way by a number of investigators. As early as 1804, Buchholz (*Gehlens Neues Journ. d. Chem.*, **3,** 7) observed that sulphur and concentrated sulphuric acid, when heated, produced a blue distillate. Vogel (*Schweigg. J.*, **4,** 121), a few years later, tried the action of sulphur on sulphur trioxide and obtained, besides the blue product, green and brown colorations. Later Schweigger (*J. Chem. u. Phys.*, **13,** 484), Berzelius (*Lehrb., Bd. I,* 485, 5th aufl.), Stein (*J. prakt. Chem.*, **6,** 172, 1838), and Wach (*Schweigg. J.*, **50,** 1) came to the conclusion that the colors produced in the reaction were due either to a mixture of sulphur and sulphur trioxide or to a solution of sulphur in sulphur trioxide.

Weber (*Pogg. Ann.*, clvi, 531) about 1875 proved that the products of the reaction included a new oxide of sulphur, sulphur sesquioxide, which he analyzed and found to have the composition S_2O_3. Weber found that this oxide decomposed completely into sulphur and sulphur dioxide at temperatures above 15°C.

The reactions for the production and decomposition of sulphur sesquioxide combined give the reaction equation at higher temperatures.

$$2SO_3 + 2S = 2S_2O_3$$
$$2S_2O_3 = S + 3SO_2$$
$$\overline{2SO_3 + S = 3SO_2}$$

This reaction read in the reverse direction. $3SO_2 = 2SO_3 + S$ perhaps represents the extreme limit of diminishing the proportion of oxygen in the action $2SO_2 + O_2 = 2SO_3$ employed commercially in the contact process for sulphuric acid production. Knietsh (*Ber.*, **34,** 4069, 1901), Bodenstein and his students (*Zeit. f. Electrochem.*, **11,** 373, 1905; *Zeit. physikal. Chem.*, **60,** 1, 1907; *ibid.*, **75,** 30, 1910, and **80,** 148, 1912) studied this latter reaction extensively. More recently Lewis and Ries (*Ind. Eng. Chem.*, **17,** 593, 1925) have studied the same reaction. Cohen and his students (*Zeit. f. Electrochem.*, **13,** 545, 1907; *Zeit. physikal. Chem.*, **70,** 88, 1910) who employed ultra-violet light in their researches have also investigated the contact process. Cohen

and Becker (*loc. cit.*) also studied the decomposition of sulphur dioxide, $3SO_2 = 2SO_3 + S$, by light, but the sulphur produced screened out the light and stopped the reaction. Deville (*Bull. Soc. Chem.*, **II, 1,** 366) passed sulphur dioxide through a porcelain tube at 1200°C. and stated that sulphur and sulphur trioxide were formed. Opposing this idea, Nernst (*Zeit. f. Electrochem.*, **9,** 622, 1903) found that the molecular weight of sulphur dioxide was normal at 1950°C.

The foregoing evidence shows that the reaction $S + 2SO_3 = 3SO_2$ is exothermic with the production of SO_2, is not reversible with rise in temperature as would normally be expected and predicted, but is reversible under the influence of ultra-violet light.

Practically all of the work dealing with the reaction $2SO_3 + S = 3SO_2$ has been qualitative. Hence specific heats, heats of formation, equilibrium constants and similar critical data are meager, or are lacking entirely. This research is an attempt to make quantitative measurements which would allow computation of some of these data.

Objectives Undertaken

The immediate objects in view in this investigation were:

1. To determine the equilibrium constant, at two or more temperatures, for the reaction $S + 2SO_3 = 3SO_2$.
2. To calculate critical thermal data as far as the results of the research would permit.

In this investigation all measurements were made at, or above, the temperature of boiling sulphur. This was done, not only to avoid the complications arising from working with a two-phase system, but also to avoid the inclusion of indeterminate oxides mentioned above, which form when sulphur and sulphur trioxide are brought together at room temperatures. The composition of equilibrium mixtures was computed from measurements of pressure made at constant volume and temperature. Sulphur of the best quality was furnished by the J. T. Baker Chemical Co. This sulphur was redistilled before using except in a few cases where it was used as received. In every case it was dried for several days in a desiccator. The contact process was employed for the preparation of the sulphur trioxide. In all of this work only Pyrex glass was used.

Apparatus and Experimental Procedure

The apparatus employed (see Figure I) throughout the investigation was similar in every detail to that used by Lewis and Randall (*J. Am. Chem. Soc.*, **40,** 362, 1918) in the determination of the equilibrium between water and sulphur at the boiling point of sulphur. The reacting materials, sulphur trioxide, contained in a sealed tube, F, and sulphur, were placed in the glass reaction chamber A of about 350 cc. capacity, connected through the capillary tube D to the open manometer M. By means of the leveling

device P the level of the mercury in the short arm of the manometer could always be brought to the mark E, near the end of the capillary D. Before evacuation of the reaction chamber the level of the mercury was brought below the side arm L. The apparatus was evacuated through the side arm L by means of a Cenco Hyvac pump (not shown in the figure). When a

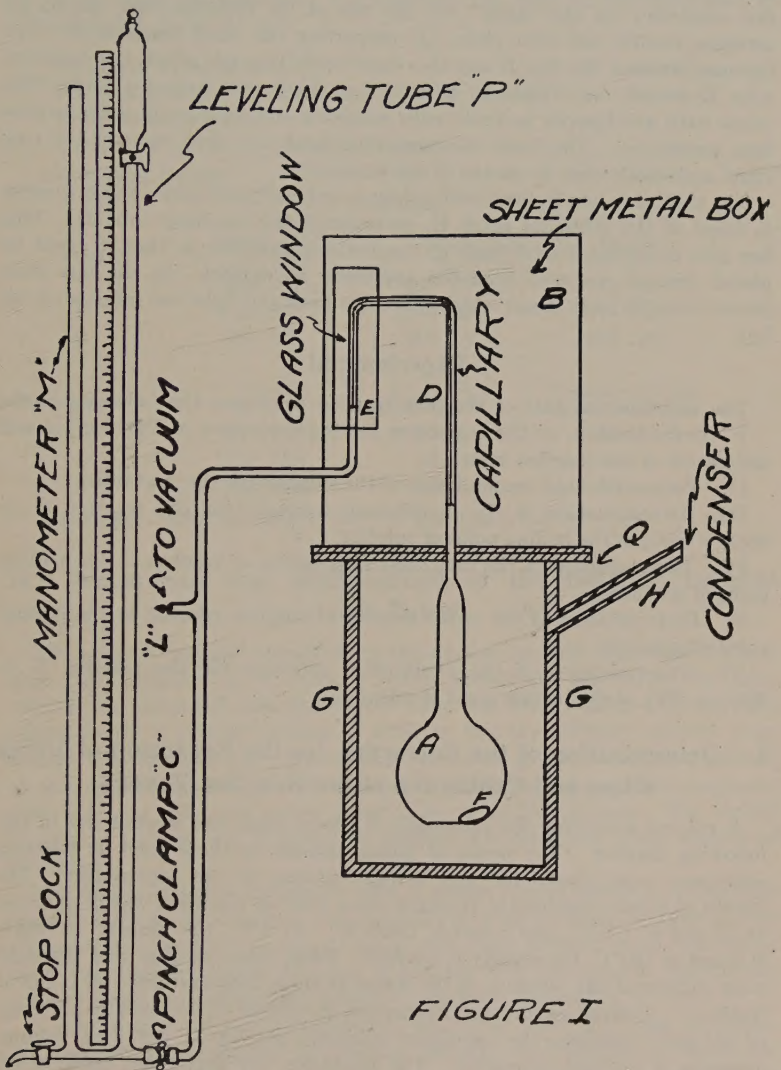

FIGURE I

vacuum of approximately 0.001 mm. had been obtained the sidearm L was sealed. The screw clamp C, operated on a short section of rubber tubing, enabled a control of the mercury level in the manometer during the attainment of equilibrium, but was always left open during the final readings on the scale S.

The reaction chamber was heated by means of a bath of sulphur or selenium vapor, depending on the temperature desired. This bath GG consisted of a steel cylinder six inches in diameter and about twelve inches high, with a welded bottom. Near the top of this cylinder a piece of iron pipe, H, one-half inch in diameter and ten inches long, was screwed in and served as a reflux condenser for the vapor. On the top of the cylinder were placed an asbestos washer and iron plate, Q, supporting the sheet iron box B. The opening between the box B and the vapor bath through which the capillary tube D passed, was closed by means of packing with asbestos cord. The vapor bath was heavily jacketed with magnesia and asbestos in order to give heat protection. The bath was supported by heavy iron rings and a ring stand and was heated by means of gas burners.

The sheet iron box B, lined with asbestos and equipped with a small window in front of the reference mark E, surrounded the capillary tube D. This box was constructed with slots in the bottom and side so that it could be placed over or removed from the apparatus as desired. In the box were placed two 100 watt lamps which served to heat and light the interior of the box.

Experimental

The experimental part of the investigation comprises the following parts:

I. Determination of the correction for the expansion of Pyrex glass and calibration of the reaction vessel.

II. Preparation and manipulation of the sulphur trioxide and tubes.

III. Determination of the equilibrium constant for the reaction $S + 2SO_3 = 3SO_2$ at the boiling point of sulphur.

IV. Determination of the molccular aggregation of sulphur at the boiling point of selenium.

V. Determination of the vapor density of sulphur trioxide at the boiling point of selenium.

VI. Determination of the equilibrium constant for the reaction $S + 2SO_3 = 3SO_2$ at the boiling point of selenium.

I. Determination of the Correction for the Expansion of Pyrex Glass and Calibration of the Reaction Vessel

A volume correction for expansion of Pyrex glass was worked out in the following manner. The necks of flasks, similar to those used as reaction chambers, were constricted and a mark placed on the constriction. The weight of water contained in the flask when filled to the mark was determined at 4° and at 100°C. (see *a* and *b*, Table I). At 4°C. the density of water is 1 and at 100°C. the density is 0.95838. From these weights and densities were computed the volumes of the flasks at these temperatures (see *c* and *d*, Table I). Column *e* expresses the increase in volume of the flask for a change of 96° and *f* expresses the calculated expansion per 100°C. per liter volume, assuming a uniform expansion. The expansion per degree per cubic centimeter was computed from the average value of the expansion per 100°C. per liter.

At the close of each run the volume of each reaction chamber used was determined in the following manner. The reaction chamber with a small portion of capillary attached was removed, weighed empty and weighed again filled with boiled distilled water cooled to room temperature. From

the weight of the water the volume was determined by dividing by the density of water at the given temperature. An attempt was made to correct for residual sulphur but the correction was so small and uncertain that it was omitted. The correction for the expansion of glass was calculated for the size of the flask and the temperature range and added to the volume determined for room temperature. For example, the data for the flask used in Experiment 1, Table II are:

Weight of water at 25°C.	348.08 gm.
Vol. of flask at 25°C. (water corrected for density)	349.12 cc.
Temperature range	419.7°
Correction = $419.7 \times 349.12 \times 1.243 \times 10^{-5}$ =	1.82 cc.
Corrected volume	350.94 cc.

TABLE I

Flask	*a* Weight H_2O at 4°C.	*b* Weight H_2O at 100°C.	*c* Volume at 4°C.
1	940.70 gm.	902.55 gm.	940.705 cc.
2	1119.78	1074.58	1119.788
3	938.26	900.16	938.268

Flask	*d* Volume at 100°C.	*e* Expansion Cc. per 96°C.	*f* Expansion Cc. per Liter per 100°C.
1	941.756 cc.	1.05 cc.	1.20 cc.
2	1121.250	1.46	1.16
3	939.335	1.06	1.35

Average: 1.243, or 1.243×10^{-5} cc. per degree per cc.

II. Preparation and Manipulation of the Sulphur Trioxide and Tubes

The sulphur trioxide, prepared by the contact process, was collected in a glass tube immersed in ice water. About double the amount of the oxide needed was collected, one end of the tube was then sealed, and the tube placed under a partial vacuum in order to free the sulphur trioxide from sulphur dioxide and air. When what appeared to be the desired amount of sulphur trioxide still remained (usually about half the amount originally collected), the tube was sealed while under a partial vacuum. The weight of sulphur trioxide was obtained by difference in final and initial weights of the tube.

The manipulation of the sealed tube F merits special mention. This tube must be sufficiently strong to withstand the internal pressure developed when the reaction vessel is evacuated, yet at the right moment must rupture to allow the sulphur trioxide to come in contact with the sulphur and do this without explosion sufficiently violent to wreck the apparatus.

A large number of runs were failures, due to the violence of the explosion. To eliminate this difficulty, the sulphur trioxide was collected as before but a three limbed tube was used. Previous to collecting sulphur trioxide one of these limbs was sealed with a sulphur plug which would hold the sulphur trioxide in the tube until a temperature of about 120° was attained, when the melting sulphur allowed the escape of the sulphur trioxide. The sulphur would withstand the action of the sulphur trioxide long enough to act effectively as a seal for from five to eight hours. A somewhat better plan was

devised during the work at the boiling point of selenium. The sulphur trioxide was collected and sealed in a three limbed tube, one limb of which was drawn out to a fine capillary. The capillary could be broken by gently shaking the apparatus, thus bringing the sulphur and sulphur trioxide together at the desired time. This latter plan was considered better, for it furnished a means of placing the sulphur trioxide alone in the reaction chamber and eliminated any chance of the sulphur plug reacting with the sulphur trioxide during the collecting process. This reaction, however, at temperatures around 0 °C. is apparently very slight.

III. Determination of the Equilibrium Constant for the Reaction $S + 2SO_3 = 3SO_2$ at the Boiling Point of Suphur

Three grams of the redistilled and dried sulphur was placed in the reaction chamber together with one of the tubes of sulphur trioxide (prepared as described above). This quantity of sulphur was sufficient to allow an excess throughout the reaction. The apparatus was then evacuated, and placed in the vapor bath as indicated in Figure I. The temperature of the vapor bath was slowly raised and the lights in the box B were switched on. Early in the course of this heating the sulphur plug in the sulphur trioxide tube melted and allowed the sulphur trioxide to react with the sulphur. At frequent intervals the clamp C was opened and the mercury level adjusted to the reference mark. At the time the pressure in the chamber had apparently reached equilibrium, the height of mercury on the scale S was read, the height of the reference mark E determined by means of a cathetometer and the barometer reading recorded. When five consecutive readings, taken at five minute intervals, which did not vary by more than one-tenth of a millimeter, were secured, equilibrium was considered to have been attained. The total pressure P on the system is equal to the barometric pressure plus the difference in height of the mercury in the two arms. From this total pressure P the composition of the equilibrium mixture was computed in the following manner suggested by Randall and Bichowsky (*J. Am. Chem. Soc.*, **40,** 368, 1918) in connection with their study of the action of water on sulphur. At equilibrium:

$P = P_S + P_{SO_2} + P_{SO_3}$, where 1

P = Total observed pressure at equilibrium,

P_S = Final pressure due to sulphur = atmospheric pressure = barometric pressure,

P_{SO_2} = Final pressure due to sulphur dioxide,

P_{SO_3} = Final pressure due to sulphur trioxide.

Also, $P - P_S = P_{SO_2} + P_{SO_3}$. 2

Let P_c = Calculated pressure of sulphur trioxide if no action occurred, assuming gas laws to hold,

x = Pressure loss due to sulphur trioxide reacting.

Then, $P_c - x = P_{SO_3}$ (defined above) 3

And $1.5x = P_{SO_2}$ (defined above). 4

Since, in the reaction $S + 2SO_3 = 3SO_2$, the pressure of the sulphur is constant and equal to atmospheric pressure, and since in this reaction the change is from two volumes of sulphur trioxide to three volumes of sulphur dioxide, then the pressure of the resulting sulphur dioxide, P_{SO_2}, would be 3/2, or 1.5 times that of sulphur trioxide from which it came.

And, $P_c - x + 1.5x = P_c + 0.5x = (P_{SO_2} + P_{SO_3})$ 5

Or, $x = 2(P_{SO_2} + P_{SO_2} - P_c)$. 6

Knowing the numerical value of x, the values of P_{SO_3} and P_{SO_2} are found from equations 3 and 4. The data and results for a number of experiments are found in Table II.

TABLE II

DATA FOR DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR THE REACTION $S + 2SO_3 = 3SO_2$ AT THE BOILING POINT OF SULPHUR

PART A:

Run	*a* Initial Weight of SO_3	*b* Volume of Flask	*c* Total Observed Press. P
1	0.0837 gm.	350.94 cc.	95.04 cm. Hg
2	.2364	385.10	126.62
3	.5557	375.88	199.22
4	.6046	350.90	220.03
5	.7867	356.85	258.70

Run	*d* Barometer P_S	*e* Height of Mercury above E Press. of SO_2 and $SO_3 = P_{SO_2} + P_{SO_3}$
1	75.04 cm. Hg	20.00 cm. Hg
2	75.16	51.46
3	75.30	123.92
4	74.58	144.45
5	74.00	184.70

TABLE II

PART B:

Run	*f* Calc. Press. SO_3 If No Action P_c	*g* Pressure Loss of SO_3 x	*h* Final Press. of SO_2 P_{SO_2}	*i* Final Press. of SO_3 P_{SO_3}
1	13.34 cm. Hg	13.322 cm. Hg	19.983 cm. Hg	0.017 cm. Hg
2	34.33	34.254	51.381	.079
3	82.69	82.464	123.696	.224
4	96.40	96.108	144.162	.288
5	123.30	122.796	184.194	.506

Run	Equilibrium Constant K_p
1	2.98×10^5
2	1.83×10^5
3	2.14×10^5
4	1.88×10^5
5	1.10×10^5
Average	1.985×10^5

Maximum Variation, $0.995 \times 10^5 = 50.1\%$

Average Variation, $0.429 \times 10^5 = 22\%$

The equilibrium constant, K_p, was obtained by changing the pressures in the table to partial pressures by dividing by the total pressure and substituting these values in the equation:

$$K_p = \frac{(p_{SO_2})^3}{(p_{SO_3})^2 \times (p_{S_8})^{1/8}}$$

where p_{SO_2} represents the partial pressure of sulphur dioxide, p_{SO_3} the partial pressure of sulphur trioxide, and p_{S_8} the partial pressure of sulphur.

In the calculation of the equilibrium constant the number of atoms of sulphur in a molecule was taken as eight, since Preuner and Schupp (*Z. Physikal. Chem.*, **39**, 322, 1902) found sulphur at its boiling point to be mainly a mixture of S_6 and S_8, with S_8 in excess over S_6.

IV. Determination of Molecular Aggregation of Sulphur

An indication of the state of molecular aggregation of sulphur vapor at the temperature of boiling selenium was gained by vapor density determination. The apparatus and experimental manipulation were the same as described in the general procedure with the exception that sulphur was the only substance in the reaction vessel. The results of a number of determinations are shown in Table III.

The molecular weight of sulphur was calculated from $PV = nRT$, or $n = g/m$, or $PV = (g/m)RT$ and $m = gRT/PV$, where m is the molecular weight of sulphur and g is the weight of the sample in grams. The number of atoms of sulphur per molecule, or $m/32 = x$, was calculated by dividing the determined molecular weight by the atomic weight of sulphur.

TABLE III

DATA AND RESULTS FOR THE DETERMINATION OF MOLECULAR AGGREGATION OF SULPHUR

a Wt. of Sulphur	*b* Volume of Flask	*c* Total Obs. Press.	*d* m = Wt. of 22.4 l. at S. T. P.	*e* No. of Atoms per Molecule x for S_x
1.0311 gm.	299.58 cc.	107.59 cm. Hg	192.16	6.005
1.2294	392.38	99.06	190.08	5.940
0.9928	345.23	90.28	191.06	5.980
1.0113	330.22	96.04	191.42	5.985
			Average	5.978

V. Determination of the Vapor Density of Sulphur Trioxide at the Boiling Point of Selenium

Tubes drawn to a fine capillary, containing sulphur trioxide, were placed in the reaction chamber. After exhaustion and the adjustment of the mercury level, the reaction chamber was shaken gently in order to break the capillary tip and allow the sulphur trioxide to escape. Otherwise the procedure was the same as in the general case. The data at equilibrium temperature are recorded in Table IV.

Let P = the observed pressure,

P_c = the calculated pressure of sulphur trioxide for no dissociation,

Then, $P - P_c = P_{O_2}$, pressure due to oxygen, assuming the reaction $SO_3 = SO_2 + {}^1/_2O_2$, since the increase in pressure over the theoretically calculated pressure is due to the oxygen formed, because there are the same number of molecules of sulphur dioxide formed as of sulphur trioxide consumed. Then the pressure exerted by sulphur dioxide, P_{SO_2}, is equal to twice P_{O_2}, since for every half mol of oxygen formed one mol of sulphur dioxide is formed. The pressure of sulphur trioxide, P_{SO_3}, is equal to the total observed pressure less the combined pressures of the other gases, or,

$$P_{SO_3} = P - (P_{O_2} + P_{SO_2})$$

m = the weight of 22.4 liters of the gas at standard conditions and was calculated upon the assumption that the gas laws hold.

TABLE IV

DATA AND RESULTS FOR DISSOCIATION OF SULPHUR TRIOXIDE

Run	*a* Initial Wt. of SO_3	*b* Volume of Flask	*c* Total Observed Pressure P	*d* Calculated Pressure P_c
1	0.1168 gm.	161.38 cc.	59.66 cm. Hg	54.34 cm. Hg
2	.4546	379.85	95.005	89.57
3	.3910	352.45	89.10	82.39

Run	*e* Pressure of O_2 P_{O_2}	*f* Pressure of SO_2 P_{SO_2}	*g* Pressure of SO_3 P_{SO_3}	*h* Density, m = Wt. of 22.4 Liters at S. T. P.
1	5.320 cm. Hg	10.64 cm. Hg	43.70 cm. Hg	72.69
2	5.144	10.280	79.57	75.66
3	6.75	13.50	68.85	74.77

Run	*i* Dissociation Constant K_p
1	0.07221
2	.0300
3	.0539
Average	.0520

The dissociation constant for the reaction $SO_3 = SO_2 + {}^1/_2O_2$ was calculated by converting the pressures of the gases concerned into their partial pressures and substituting in the equation:

$$K_p = \frac{(p_{SO_2}) \times (p_{O_2})^{1/2}}{(p_{SO_3})}$$

This was all done in a single step.

VI. Determination of the Equilibrium Constant for the Reaction $S + 2SO_3 = 3SO_2$ at the Boiling Point of Selenium

Sulphur and a sealed tube of sulphur trioxide were placed in the reaction chamber and after exhaustion the capillary tip was broken. The general procedure was then followed. The data for the reaction are given in Table V.

The data in the third part of the table were obtained for a set of equations similar to those of Randall and Bichowsky (*J. Am. Chem. Soc.*, **40**, 368, 1918) worked out in the calculation of pressures of mixtures of gases in the reaction between water and sulphur.

Let P = the total observed pressure at equilibrium,

P_a = the theoretical pressure of sulphur trioxide for no action, assuming the gas laws to hold,

P_b = the theoretical pressure of sulphur as S_6 for no action, assuming the gas laws to hold,

x = the decrease in pressure due to sulphur used.

Then $12x$ is the decrease in pressure due to sulphur trioxide used, since

the volume of sulphur trioxide consumed in the reaction $^1/_6S_6 + 2SO_3 = 3SO_2$ is twelve times the volume of sulphur consumed.

Then $P_a - 12x$ = final pressure, P_{SO_3}, of sulphur trioxide 1

$P_b - x$ = final pressure, P_S, of sulphur 2

And $18x$ = final pressure of sulphur dioxide, P_{SO_2} 3

because for every volume of sulphur used 18 volumes of sulphur dioxide is formed.

At equilibrium $P_{SO_3} + P_S + P_{SO_2} = P$ 4

Then $P_a - 12x + P_b - x + 18x = P$ 5

Or $P_a + P_b + 5x = P$ 6

$$x = \frac{P - (P_a + P_b)}{5} \qquad 7$$

P_{SO_3}, P_S and P_{SO_2} are then obtained by substituting the value of x in Equations 1, 2 and 3, respectively.

K_p, the equilibrium constant, was obtained by changing the pressures of the gases in the reaction to partial pressures and substituting in the equation:

$$K_p = \frac{(p_{SO_2})^3}{(p_{S_6})^{1/6} \times (p_{SO_3})^2}$$

which is all done in one operation.

The molecular aggregation of sulphur was taken as S_6 as determined above.

TABLE V

DATA AND RESULTS AT THE BOILING POINT OF SELENIUM FOR THE REACTION $S + 2SO_3 = 3SO_2$

PART I:

Run	*a* Weight of SO_3	*b* Initial Wt. of S	*c* Vol. of Flash Corrected	*d* Total Obs. Pressure P
1	0.4719 gm.	0.8045 gm.	343.30 cc.	219.48 cm. Hg
2	.6007	.6006	369.85	223.550
3	.5325	.5386	355.20	204.594
4	.1180	.5543	352.161	84.860

PART II:

Run	*a* Pressure of SO_3 Calc. P_a	*b* Pressure of S Calc. P_b
1	103.21 cm. Hg	73.31 cm. Hg
2	121.98	50.81
3	111.35	46.91
4	25.16	49.23

PART III:

Run	*a* *x*, Press. Loss of S	*b* Final Press. of S P_S	*c* Final Press. of SO_3 P_{SO_3}	*d* Final Press. of SO_2 P_{SO_2}	*e* Equilib. Const. K_p
1	8.5920 cm. Hg	64.719 cm. Hg	0.105 cm. Hg	154.656 cm. Hg	1.247×10^6
2	10.1528	40.653	.1464	182.750	1.692×10^6
3	9.2674	37.639	.1422	166.813	1.099×10^6
4	2.0944	47.136	.0252	37.699	1.125×10^6
				Average	1.2907×10^6

Maximum variation of K_p, $0.4013 \times 10^6 = 24\%$

Average variation, $0.1605 \times 10^6 \pm 13\%$

Thermal Calculations

Free Energy: The free energy changes for the reaction between sulphur and sulphur trioxide at the boiling point of sulphur and selenium were obtained by substituting the average determined values of K_p in the equation:

$\Delta F^\circ = -RT\ln K$ (Lewis and Randall Text, p. 294) 1

Or, $^1/_8S_8 + 2SO_3 = 3SO_2$; $\Delta F^\circ_{718} = -17{,}500$ cal. 2

And, $^1/_6S_6 + 2SO_3 = 3SO_2$; $\Delta F^\circ_{963} = -27{,}080$ cal. 3

In Equation 2 sulphur appears as S_8 and in Equation 3 as S_6 but by accounting for the free energy change from $^1/_8S_8$ to $^1/_6S_6$ the equations are made comparable.

$6S(\text{rhomb.}) = S_6$; $\Delta F^\circ_{718} = -3160$ cal. (Lewis, p. 538) 4

$8S(\text{rhomb.}) = S_8$; $\Delta F^\circ_{718} = -4110$ cal. 5

Or, $S(\text{rhomb.}) = {}^1/_6S_6$; $\Delta F^\circ_{718} = -526.6$ cal. 6

$S(\text{rhomb.}) = {}^1/_8S_8$; $\Delta F^\circ_{718} = -513.7$ cal. 7

Subtracting Equation 6 from Equation 7:

$^1/_6S_6 = {}^1/_8S_8$; $\Delta F^\circ_{718} = 12.9$ cal. 8

The free energy change in Equation 8 is so small in comparison with the free energy change of the reaction between sulphur and sulphur trioxide at either of the temperatures and the accuracy of the work not of an order to warrant the consideration of such a small correction that the equation is written $^1/_6S_6 + 2SO_3 = 3SO_2$ both at 718°K. and 963°K. throughout the remainder of the discussion.

The theoretical calculation of the free energy change for the reaction $^1/_6S_6 + 2SO_3 = 3SO_2$ by ordinary free energy equation is not directly applicable because the heat capacity for neither S_6 gas nor sulphur trioxide has been determined.

However, Lewis and Randall (chapter on sulphur) have developed the following equations which may be employed in calculating free energy change.

$SO_2 + {}^1/_2O_2 = SO_3$; $\Delta F^\circ = -22{,}600 + 21.36T$ 9

This is based upon the assumption that change of heat capacity with temperature is zero (Lewis and Randall, p. 551).

$^1/_2S_2 + O_2 = SO_2$; $\Delta F^\circ = -83{,}260 + 2.751nT - 0.0028T^2 + 0.0000003T^3 + 0.9T$ (Lewis and Randall, p. 548) 10

Multiplying Equation 9 by two and subtracting the result from Equation 10:

$^1/_2S_2 + 2SO_3 = 3SO_2$, $\Delta F^\circ = -38{,}060 + 2.75T\ln T - 0.0028T^2 - 0.00000031T^3 - 41.82T$ 11

Substituting T = 718 and 963 in Equation 11:

$^1/_2S_2 + 2SO_3 = 3SO_2$, $\Delta F^\circ_{718} = -56{,}600$ cal. 12

$^1/_2S_2 + 2SO_3 = 3SO_2$, $\Delta F^\circ_{963} = -63{,}000$ cal. 13

But $^1/_2S_2$ must be replaced by $^1/_6S_6$.

Equations from Lewis and Randall, p. 537–538:

$2S(\text{rhomb.}) = S_2$, $\Delta F^\circ_{718} = 3320$ cal. 14

$6S(\text{rhomb.}) = S_6$; $\Delta F^\circ_{718} = -3160$ cal. 15

Dividing Equation 14 by two and Equation 15 by six:

$S(\text{rhomb.}) = {}^1/_2S_2$; $\Delta F^\circ_{718} = 1660$ cal. 16

$S(\text{rhomb.}) = {}^1/_6S_6$; $\Delta F^\circ_{718} = -532$ cal. 17

Subtracting 17 from 16:

$^1/_6S_6 = {}^1/_2S_2$; $\Delta F^\circ_{718} = 2192$ cal. 18

Adding 18 and 12:

$^1/_6S_6 + 2SO_3 = 3SO_2$; $\Delta F^\circ = -54{,}400$ cal. 19

In the absence of an exact means of calculating the free energy change for

the reaction $^1/_6S_6 = {}^1/_2S_2$ at 963°K., 2200 calories are also added to the free energy Equation 13, giving:

$$^1/_6S_6 + 2SO_3 = 3SO_2; \quad \Delta F° = -60{,}800 \text{ cal.}$$

Change of Heat Content: Substituting in the vant Hoff equation:

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \text{ or } \Delta H = \frac{RT^2 d\ln K}{dT} \text{ (Lewis and Randall, p. 298)}$$

$d\ln K = 2.303 \times 0.81306$
$dT = 963 - 718 = 245°C.$

$$\Delta H_{718} = \frac{1.9885 \times 2.303 \times 0.81306 \times (718)^2}{245} = 7520 \text{ cal.}$$

$$\Delta H_{963} = \frac{1.9885 \times 2.303 \times 0.81306 \times (963)^2}{245} = 13{,}210 \text{ cal.}$$

Table VI

Table of Thermal Results

$\Delta F°$ Experimental	$\Delta F°$ Calculated	ΔH Determined Experimentally
718°K. —17,500 cal.	—54,400 cal.	7520 cal.
963°K. —27,080	—60,800	13,210

Discussion

The values of the free energy change determined in this investigation, Table VI, and those calculated from the best available data agree in sign and order of magnitude. In developing the equations used in these calculations, Lewis and Randall (chapter on sulphur) have employed the results of a large number of investigators, spread over a considerable period of time and have made the assumption that the change in heat capacity for the reaction $SO_2 + {}^1/_2O_2 = SO_3$ is equal to zero. Values calculated by such a roundabout means probably would not be expected to agree closely with those determined by the most direct method available, which was employed in this investigation.

In most chemical reactions ΔH (the change in heat content) and ΔF (the free energy change) have the same sign. ΔF and ΔH are related to each other by the equation:

$$\Delta F = \Delta H - T\Delta S \text{ (Lewis and Randall, p. 169)}$$

In this work ΔF and ΔH are found to be opposite in sign. Mathematically, this condition can be gained from Equation 1 by making $T\Delta S$ (the product of the absolute temperature and the entropy change) large in comparison with ΔH. Since the work was carried out at a fairly high temperature and ΔS is positive for a spontaneous chemical change, $T\Delta S$ is easily seen to be a large positive number.

Although the method used in this investigation is peculiarly adapted to the study of the reaction: $^1/_6S_6 + 2SO_3 = 3SO_2$ at the boiling point of sulphur because the pressure of sulphur is obtained from the barometer reading and only the two other pressures are calculated, the values of K_p show a wider variation among themselves than at the boiling point of selenium.

This is partly due, perhaps, to the fact that at the higher temperature a glass sealed tube was used for the sulphur trioxide, while at the boiling point of sulphur the tubes with the sulphur plug were employed. The reaction between sulphur and sulphur trioxide at temperatures around 0 °C. (temperature at which sulphur trioxide was collected) is apparently very slow. It may be sufficient to account for greater variation in the values of K_p at the boiling point of sulphur.

In the calculation of K_p at the boiling point of selenium sulphur is taken as S_6 in accordance with the results obtained in this work in the determination of the molecular aggregation of sulphur. The value given by Blitz and Preuner (*Z. f. Physikal. Chem.*, **39**, 322, 1902) is about S_4 at the temperature and pressure in question; however, for this apparatus, pressure and temperature the value S_6 seems to be more exact as shown by the results given in Table III.

Upon consideration of the fact that in the reaction between sulphur and sulphur trioxide the free energy change $\Delta F^\circ = -27{,}080$, the dissociation of sulphur trioxide is not likely to take place to any great extent because the free energy change

$$2SO_3 = 2SO_2 + {}^1/_2O_2;$$
$$\Delta F^\circ_{963} = -RT\ln K \times 0.052 = -1.9885 \times 2.303 \times 963 \times \log 0.052 = 12{,}000 \text{ cal.}$$

A reaction liberating the larger amount of free energy will proceed at the expense of one absorbing energy. This being the case, the reaction between sulphur and sulphur trioxide would eliminate the dissociation of sulphur trioxide. Furthermore, the concentration of sulphur trioxide at the end is low compared to the concentration of sulphur dioxide, which would also tend to prevent the dissociation of sulphur trioxide, according to the equation $SO_3 = SO_2 + {}^1/_2O_2$, and although the vapor density of sulphur trioxide at the boiling point of selenium was found to be less than normal, the reasonable thing to believe is that this would not make any serious error in the values of K_p.

Considering the difficulties in manipulation, the large number of independent operations and the fact that the assumption is made that the gas laws hold for the gases concerned, the agreement for the values of K_p at the temperatures of the investigation is quite satisfactory.

The free energy data for a reaction are an important factor in predicting the extent to which a reaction proceeds, or whether it will go at all, under a definite set of conditions. Furthermore, from such data may be determined which reaction will take place, if there is more than one possibility. Chemists are coming more and more to look for such data. With a knowledge of the equilibrium constant and the value of the heat content at a given temperature the value of the equilibrium constant at any given temperature may be calculated.

Summary and Conclusions

1. The reduction of sulphur trioxide by sulphur has been studied by the best available method.

2. The equilibrium constant for the reaction has been determined at the boiling point of sulphur and of selenium.

3. The free energy change at the two temperatures mentioned has been calculated.

4. The change in heat content has been computed.

5. Sufficient data have been obtained to predict the extent of the reaction at any given temperature.

6. From the data obtained it is evident that (*a*) the reaction proceeds well toward completion at both temperatures employed in this study; (*b*) the reaction proceeds further toward completion at the higher temperature.

Biography

William Ralph Skidmore was born at Comstock, Oregon, on July 20, 1895. His early education was obtained in the rural schools and the Cottage Grove, Oregon, High School. In 1915 he entered the University of Oregon and received the B.A. degree in 1920, after having served sixteen months with the A. E. F. in France. Work as a graduate assistant was continued until 1922 at Oregon, when the M.A. degree was conferred. Since then he has been a graduate assistant in the State University of Iowa.

He is a member of Sigma Xi, Gamma Alpha and the American Chemical Society.